

**REMARKS**

Applicants respectfully request reconsideration of the present application in view of the foregoing amendments and in view of the reasons that follow. The amendment to claim 1 is supported by page 7, lines 15-20 and Examples 1-3 on page 9 of the specification.

**Rejections Under 35 USC 102(b)**

Applicants traverse the rejections under 35USC 102(b) for the following reasons.

*Hayden (US 5,387,751)*

The catalyst used in Hayden is a silver catalyst supported on  $\alpha$ -alunima, which was calcined before use (see at lines 7 to 11, col. 3, and lines 52 to 53, col. 6). Hayden teaches that the catalyst is dried before use. The process of Hayden is silent on the utilization of water vapor in the epoxidation process. See the Examples.

In Example 17, a process gas stream containing 30% propylene, 8% oxygen and 1150 ppm dichloromethane was used and the reaction was performed with oxygen selectivity/conv. of 14%/12% and 35%/6% as shown in Table 6, col. 13. The amount of oxygen that was used for undesirable side reactions other than epoxydation reaction is calculated to be less than 1%. Then the amount of water that may have resulted from such oxygen per mol of propylene in the process gas stream, or in the reaction would be far less than the recited amount in the present claim.

The Examiner mentions the chlorine-containing reaction modifier such as a Cl-C10 compound. However, it is stated that the concentration of such compound should be in the range of 0.1 to 500 parts per million parts of the reaction medium by weight. The amount of the modifier is too much small to render the presently claimed amount of water anticipated.

Hayden does not teach or disclose the amount of water that was added to the reaction in the presently claimed process either explicitly or inherently.

*Boeck (US 5,618,954)*

The process of Boeck is directed to epoxidation of butadiene using a catalyst containing Ag supported on  $\alpha$ -alumina (penultimate paragraph col. 7). Boeck is silent on propylene and therefore cannot anticipate the present claims.

*Nakashiro (US 6,498,122)*

The process of Nakashiro is directed to the epoxidation of ethylene. Nakashiro is silent on propylene. Superheated steam is applied to the impregnated carrier to make the distribution of silver and alkali metal supported in the resulting catalyst uniform as described at lines 46 to 49, col. 4. But the production of ethylene oxide is not conducted in the presence of such superheated steam.

In connection with Boeck and Nakashiro, the applicants attach hereto as Appendix I Applied Catalysis A: General 221 (2001) 73-91 by Monnier. Monnier discloses under 3.2. Epoxidation of 1,3-butadiene, from the last paragraph on page 82 to line 5, on the right column, p.83, in Table 2 that Ag catalyst in which Ag is supported on  $\alpha$ -alumina shows catalytic activity for oxidation of butadiene and ethylene having vinyl hydrogens only but is not suitable to epoxidize propylene and butene having allyl hydrogen atoms. In the disclosed reactions, ethylene and butadiene were converted to corresponding epoxy compounds. Propylene and butene, however, were not effectively converted to corresponding epoxy compounds.

Monnier teaches that the Ag catalyst in which Ag is supported on  $\alpha$ -alumina, which were also disclosed as preferable or typical catalyst in Hayden, Boeck, and Nakashiro, did not show similar effect to propylene though the differences between propylene and ethylene or butadiene is just one carbon atom and the nature of hydrogens. It can be said from the teachings of these references that in the real epoxidation reactions propylene behaves rather in a different manner than ethylene or butadiene.

Therefore, the teachings of Boeck or Nakashiro cannot anticipate the presently claimed invention.

*Mul (US 6,392,066)*

Mul discloses the epoxidation catalyst and epoxydation reaction of ethylene, and that in the penultimate paragraph col. 7 that the feedstream may contain inert gas such as nitrogen or helium as a ballast or diluent, and mentions that carbon dioxide is not desirable in view of selectivity and should preferably be removed from the feedstream.

Water vapor is referred to in the same context in which carbon dioxide is not considered a desirable component and is to be removed.

Although during the catalyst preparation a water solution is employed it is described at the last two lines of Example 1, col. 8, that the prepared catalyst is calcined at 375°C before use.

In addition there is no mention of the addition or the effect of water vapor in the oxidation reaction as it can be seen from the descriptions (e.g. Example 5, col. 9).

The process of Mul is silent on the use of water in the epoxidation process per se and therefore, cannot anticipate the present invention.

**Conclusion**


Applicants believe that the present application is now in condition for allowance. Favorable reconsideration of the application as amended is respectfully requested. The Examiner is invited to contact the undersigned by telephone if it is felt that a telephone interview would advance the prosecution of the present application.

The Commissioner is hereby authorized to charge any additional fees which may be required regarding this application under 37 C.F.R. §§ 1.16-1.17, or credit any overpayment, to Deposit Account No. 19-0741. Should no proper payment be enclosed herewith, as by a check or credit card payment form being in the wrong amount, unsigned, post-dated, otherwise improper or informal or even entirely missing, the Commissioner is authorized to charge the unpaid amount to Deposit Account No. 19-0741. If any extensions of time are needed for timely acceptance of papers submitted herewith, Applicant hereby petitions for such extension under 37 C.F.R. §1.136 and authorizes payment of any such extensions fees to Deposit Account No. 19-0741.

Respectfully submitted,

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112 kcal/mol [4,5]. Thus, electrophilic attack by oxygen and abstraction of one of the allylic C–H bonds in propylene becomes energetically more favorable than electrophilic addition of oxygen across the C=C double bond. Once abstraction of hydrogen occurs, epoxide formation is precluded.

However, higher olefins are successfully epoxidized using indirect oxidation routes, such as the well-known peroxidation process for propylene epoxidation, whereby organic hydroperoxides or organic peroxide are reacted with propylene to produce equimolar amounts of propylene oxide and organic alcohols and organic acids, respectively. For instance, the hydroperoxidation process of propylene by *tert*-butyl hydroperoxide or ethylbenzene hydroperoxide is typically conducted in the liquid phase in the presence of high-valent, homogeneous Mo, V, or Ti catalysts at 90–150 °C and 15–65 bar pressure to produce propylene oxide along with *tert*-butyl alcohol or ethylbenzene [6]. The *tert*-butyl hydroperoxide or ethylbenzene hydroperoxide oxidants are formed *in situ* in a separate step from isobutane and ethylbenzene. This technology, which is well established and provides much of the commercially-produced propylene oxide, suffers from the fact that the co-products formed during reaction are actually produced in a greater weight fraction than propylene oxide. Thus, successful application of this technology requires utilization of the by-product stream. Similarly, use of peroxide acid to oxidize propylene to propylene oxide [4] requires an outlet for the acetic acid by-product. It also needs an inexpensive source of acetaldehydic which is oxidized to form the peroxide acid.

The discovery of the titanum silicate TS-1 by Terasawa et al. [7] opened a new pathway for the epoxidation of higher olefins by permitting the use of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as the indirect oxidant to epoxidize allylic olefins and to form only H<sub>2</sub>O as an environmentally-friendly by-product [8,9]. This process is very selective to epoxides such as propylene oxides with selectivities >95%, based on propylene, and 70–95% based on H<sub>2</sub>O<sub>2</sub>. However, because of the relatively high cost of H<sub>2</sub>O<sub>2</sub>, this process has not been commercialized to date on a large scale.

Consequently, most current research and development has focused on either the use of molecular O<sub>2</sub> as the direct oxidant for selective epoxidation or on *in situ* generation of indirect oxidants, such as H<sub>2</sub>O<sub>2</sub>,

which also employs molecular O<sub>2</sub> and generates only H<sub>2</sub>O as the by-product. Quite simply, it is recognized that the least expensive oxidant for producing epoxides is molecular oxygen and that capital expenses required to construct commercial manufacturing facilities are typically lower for those processes that use molecular O<sub>2</sub>. Thus, in this report, we will discuss those catalysts and processes that either use molecular oxygen as the direct oxidant or involve O<sub>2</sub> to form *in situ* oxidants to produce higher olefin epoxides. The silver-catalyzed epoxidation of ethylene using O<sub>2</sub> will not be discussed in this report, except to provide reference for those examples that also use silver catalysts for the epoxidation of higher olefins.

## 2. Epoxidation by *in situ* generation of oxidant using O<sub>2</sub>

### 2.1. Epoxidation using transition metal complexes

Most of the earlier efforts using molecular oxygen as the *in situ* oxidant for higher olefin epoxidation have been conducted in the liquid phase using soluble metal complexes as homogeneous catalysts. Selected examples of these catalysts and performance are summarized in Table 1. Examples that require the use of non-olefin reactants, such as aldehydes, that themselves undergo oxidation, are not included, since these examples are the same as epoxidation using peroxide. In these examples cited in Table 1, most of the mechanistic schemes involve epoxidation by free radical processes involving peroxide and hydroperoxide in solution. Thus, the overall performance is the sum of both a catalytic as well as a thermal, free radical component, making it difficult to determine the efficacy of the homogeneous catalyst. For instance, Budnik and Kochi [10] reported that when Co(III) acetylacetonate was used as the catalyst during the epoxidation of norbornene and *tert*-butyl ethylene, the epoxidation reactions showed induction periods characteristic of radical chain processes, in this case  $\beta$ -peroxyethyl radicals. In these cases, the primary mechanism for olefin epoxide formation is not catalytic, but is thermal autoxidation. As is typical of most reactions proceeding by free radical mechanisms, selectivities to the olefin epoxides are often unacceptably low and the number of different products too large to make



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# The direct epoxidation of higher olefins using molecular oxygen

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## Abstract

Recent developments in olefin epoxidation have shown promising results indicating that higher olefins can be directly epoxidized using molecular oxygen, or indirectly, by using molecular oxygen to generate an active and selective oxidant *in situ* during reaction. Indirect approaches have utilized bifunctional catalysts that combine new catalyst components that generate such oxidants as H<sub>2</sub>O<sub>2</sub> *in situ* with the functional component that activates H<sub>2</sub>O<sub>2</sub> for olefin epoxidation. This approach is currently limited by the low rates of *in situ* generation of H<sub>2</sub>O<sub>2</sub> and subsequent low rates of olefin epoxide formation. Heavily-modified, silver catalysts have also shown promise as catalysts for propylene epoxidation. These catalysts contain much higher silver and alkali and alkaline earth metal loadings than their analogs used for ethylene epoxidation and are quite different in terms of their chemical and physical properties. Currently, these compositions exhibit activities and selectivities to propylene oxide that are too low for commercial applications, although further research and development may further improve catalyst performance.

Silver-based catalysts have also been used to epoxidize a wide variety of higher olefins, such as 1,3-butadiene, that do not contain allylic hydrogen atoms, or higher olefins that contain non-reactive allylic hydrogen atoms, such as norbornene. Silver-based catalysts used for selective epoxidation of non-allylic, or kinetically hindered olefins require promoters, typically cesium, rubidium, or thallium salts, to assist in the description of the olefin epoxide. Such catalysts are extremely active, selective, and stable under extended reaction conditions. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Epoxidation; Silver; Molecular oxygen; Hydrogen peroxide; Titanium silicate; Propylene; Butadiene; Promoter; Oxide; Publisher: Alkali promoters

## 1. Introduction

The epoxidation of olefins is an extremely important class of catalytic reaction in the chemical industry. The silver-catalyzed, gas phase epoxidation of ethylene using molecular oxygen is one of the now successful examples of heterogeneous catalysis to date. In 1998, the domestic production of ethylene oxide alone was 8.14 billion lbs [1]. In spite of the versatility and importance of olefin epoxides in the chemical processing industry, until very recently, no other olefins had been commercially epoxidized *in-*

ing only molecular oxygen as the oxidant. In early 1997, Eastman Chemical Company began production of 3,4-epoxy-1-butene (EBEB), the product from mono-epoxidation of 1,3-butadiene, at the tens-of-thousands scale of production [2,3]. Efforts to directly epoxidize other higher olefins, such as propylene, to their corresponding epoxides using molecular oxygen in a commercially-viable process have not been as successful. Many explanations have been proposed for the failure to directly epoxidize allylic olefins, such as propylene, to their corresponding epoxides, although the most obvious reason is the reactivity of allylic C–H bonds. The bond dissociation energy of the allylic C–H bond in propylene is 77 kcal/mol, while the vinylic C–H bond strength in ethylene is

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epoxidation economically viable. For these examples employing soluble Cu(I) and Pt(II) complexes as catalysts, however, no free radical process was operative in either case. However, both  $C_3H_6$  conversions and propylene oxide selectivities were unacceptably low in both instances, typical for catalytic, olefin epoxidation reactions using soluble, transition metal complexes. Similarly, the complex system employing  $EuCl_3$ , Zn powder, and  $CF_3COOH$  as catalyst combination results in 1-benzene epoxide formation at a turn over frequency of  $13.8 h^{-1}$ . Clearly, the data reported in Table 1 indicate the problems often cited for the use of liquid phase, olefin epoxidation reactions. The catalytic reactions are slow, giving unacceptable rates of epoxide formation; further, it is difficult to suppress free radical, chain reactions from occurring in solution. While radical reactions are much faster, they are inherently non-selective, leading to poor utilization of olefin feedstock and expensive separation processes to isolate the desired epoxide product. A much more complete discussion of transition metal complexes as olefin epoxidation catalysts has been compiled in an excellent review by Jergenson [16].

## 2.2. Epoxidation using molten salts

A very different method for propylene epoxidation has been reported by workers at Olin Corporation [17,18]. Molten salt mixtures, with  $LiNO_3$ ,  $NaNO_3$ , and  $KNO_3$  being the preferred alkali metal nitrate salts, were used to assist in the epoxidation of a vapor phase feed consisting of propylene, oxygen and nitrogen at temperatures ranging from 180 to 400 °C. While the specific nature of the catalytic activity of the molten salts is not specified nor has it been confirmed, it is believed that propylene oxide is primarily formed by the thermal reaction of propylene with oxygen, and the primary role of the molten salts is to function as a high capacity, heat removal medium, which essentially maintains an isothermal temperature profile during the highly exothermic, selective and non-selective oxidation reactions. The reaction products, which are gas stripped from the molten salt bed, are primarily composed of propylene oxide, acrolein, allyl alcohol, and acetone as well as CO and  $CO_2$ . For example, using a molten bed composition of 30 mol%  $LiNO_3$ , 20 mol%  $NaNO_3$ , and 50 mol%  $KNO_3$  at a reaction temperature of 225 °C and 338 psig pressure,

a feedstock consisting of 53%  $C_3H_6$ , 8%  $O_2$ , and balance  $N_2$  (total flow = 2000 cm<sup>3</sup>/min (STP)) was partially converted to 57% propylene oxide, 7% other  $C_3$ -oxygenates, and balance  $CO/CO_2$ ; conversion of  $C_3H_6$  was 9.7%. It is difficult to tailor the nature of the catalyst formed by the mixture of the molten salts, although the selectivity to PO does seem higher than normal for a purely thermal, even isothermal, oxidation reaction. The reaction is run lean in molecular  $O_2$ , which does suggest that the reaction may be largely thermal in nature, and that selectivity is controlled by restricting  $O_2$  concentration in the feed. Another supporting reason that the mixed molten salts may not function as true catalysts is the basis of another patent published from Olin Corporation [19]. In this patent, Meyer claims that aldehydes, including acrolein, acrolein, and propionaldehyde, which are normally isolated in small amounts during operation of the molten bed process, may be utilized in a second reactor to effect the co-oxidation of unreacted  $C_3H_6$  with the peroxides formed by the thermal reaction of these aldehydes and  $O_2$ . Additional propylene oxide is then formed by the well-known epoxidation by peroxide, which has been mentioned above. Thus, it is now difficult to determine how much of the propylene oxide which is produced in the molten salt medium is actually formed from some unspecified catalytic reaction using molten salts and how much propylene oxide is produced from the co-oxidation of  $C_3H_6$  by peroxide, which would be formed in situ in the molten medium. Again, we have a situation, where it is difficult to determine whether higher olefins have been directly epoxidized by molecular  $O_2$ , or whether another variant of co-oxidation by hydroperoxides or peroxides have occurred yet again.

## 2.3. Gas phase epoxidation using bifunctional, heterogeneous catalysts

### 2.3.1. Palladium supported on TS-1 supports

One of the most current and promising areas of higher olefin epoxidation, which circumvents many of the uncertainties and difficulties mentioned above, involves the use of novel, bifunctional heterogeneous catalysts which apparently function by generation of in situ  $H_2O_2$  from  $H_2$  and  $O_2$ . The metallic component, which is believed to generate  $H_2O_2$ , is typically supported on  $TiO_2$ , which contains  $Ti^{IV}$  sites, which

Table 1  
Epoxidation of olefins using homogeneous catalysts

Catalyst	Reaction conditions		Olefin	Conversion (%)	Selectivity to epoxide (%)	Reference
	Temperature (°C)	Pressure (psig)				
Co(III) acetylacetonate	60-120	150	18	100	95	[10]
Ag(I) and diethers	150	650	Not given	Propylene	32-45	[11]
Mo(VI) acetylacetonate	100	30	6	Substrate	59-65	[12]
Cu(I) peroxo diethers	25	150	24	Propylene	0.1	[13]
Pt(II) bullfinch	100	600	14	Propylene	1.6	[14]
BrO <sub>3</sub> + Zn powder	40	15	1	1-Hexene	3.2	[15]

desirable surface concentration of  $Pd^{2+}$  with undesirable changes in the surface morphology of the Pd aggregates from needle-shaped to spherical. Further, since supported Pt catalysts are very active for the hydrogenation of  $C_3H_6$  to  $C_3H_8$ , excess loadings of Pt must be avoided.

Little attention has been directed to determining the site for  $C_3H_6$  interaction with the  $H_2O_2$ -activated surface. It is not clear whether there is direct interaction of gas phase  $C_3H_6$  with the Ti-O-O-H site, or whether  $C_3H_6$  is chemisorbed on the Pd or Pt surface adjacent to the  $H_2O_2$ -covered  $Ti^{4+}$  site. The latter possibility would suggest that propylene oxide formation occurs at the Pd (or Pt-Pd)- $Ti^{4+}$  interface, such as at the edges of the needle-shaped, palladium aggregates in contrast with the TS-1 surface. If this is the case, the concentration of active, bifunctional sites will be quite limited, restricting the maximum rate of propylene oxide formation. The performance of this type of catalyst indicates the difficulty in forming a bifunctional catalyst having the correct composition, morphology, and distribution of active sites to give active and selective formation of propylene oxide. Failure to maintain the proper balance of  $Pd^{2+}$  sites, Pd morphology, and concentration of Pt promoter results in a catalyst having both low activity and low selectivity. Regardless, the concept of combining the site for formation of the oxidant ( $H_2O_2$ ) with the site for olefin epoxidation is a positive step in the direction to produce propylene oxide and other higher olefins directly from  $O_2$ .

Clerici and Ingallina [22] have reported that in situ  $H_2O_2$  generation can be accomplished using an allylated anthraquinone as the oxygen carrier for  $H_2O_2$  generation, rather than  $H_2$  as the oxygen carrier. This modification is based on the current, commercial method for industrial  $H_2O_2$  generation using anthraquinone, which involves the steps of hydrogenation of anthraquinone to hydroanthraquinone followed by oxidation with  $O_2$  to liberate  $H_2O_2$  and regenerate anthraquinone. Clerici argues that the selection of TS-1 as the epoxidation catalyst, rather than  $TiO_2$ , permits the use of the realistic process and channels in TS-1 to exclude diffusion of any of the anthraquinone species into the interior of TS-1, where the epoxidation takes place between  $H_2O_2$  and the olefin. Thus, catalyst lifetime should be extended and non-selective degradation of anthraquinone species should be minimized. Clerici reports that  $C_3H_6$  is selectively epoxi-

dized to propylene oxide at 78% yield at 30°C and 1.5 h reaction time using a solution containing ethyl hydroanthraquinone,  $O_2$ ,  $C_3H_6$ , and TS-1 catalyst in methoxyphenol/ $CH_3OH$  solvent. However, this is not true in situ epoxidation, since the hydrogenation of ethyl anthraquinone by  $H_2$  and Pd/C to form ethyl hydroanthraquinone was conducted ex situ. Thus, it is not clear how the addition of  $H_2$  and Pd/C to the epoxidation reactor would affect overall performance of this process, although it is highly likely that hydrogenation of  $C_3H_6$  and reduction of  $O_2$  to form  $C_3H_8$  and  $H_2O$ , respectively, would adversely affect selectivity and activity for propylene oxide formation.

## 2.2.2. Epoxidation using $H_2$ supported on $TiO_2$

Very intriguing work recently reported by Harris and coworkers [23-26] have demonstrated that a feedstream consisting of  $C_3H_6$ ,  $O_2$ , and  $H_2$  can be selectively epoxidized to form propylene oxide using highly dispersed gold supported on  $TiO_2$ . Although gold has historically been regarded as being inactive for most catalytic reactions of interest, highly dispersed gold catalysts have been found to have exceptionally high activity for many types of oxidation reactions. In earlier work, Harris et al. [27] found that highly dispersed gold catalysts were active for CO oxidation at temperatures as low as -50°C. These results, which were reproduced by others [28], predated the discovery that  $C_3H_6$  could be selectively epoxidized to propylene oxide using  $H_2 + O_2$  as the selective oxidant. For a much more complete survey of various reactions catalyzed by supported gold catalysts, see the excellent review by Bond [29].

Harris has found that that selective epoxidation of  $C_3H_6$  occurs for gold particles supported on  $TiO_2$  when the Au particles exist as nanoscale-sized particles preferentially between 2.0 and 4.0 nm in diameter. For example, vapor phase epoxidation using 0.50 g of 0.98 wt% Au/ $TiO_2$  at 50°C in a gas mixture of  $C_3H_6/O_2/H_2/Ar = 10/10/70$  at a total flow of 33.3 cm<sup>3</sup>/min gave 99% selectivity to propylene oxide; however, conversion of  $C_3H_6$  was only 1.1%. Conversion of  $H_2$  was 3.2%, indicating much of the  $H_2$  was oxidized to  $H_2O$ , not  $H_2O_2$ . Increasing the temperature to 80°C resulted in preferential combustion of  $H_2$  and  $C_3H_6$  to  $H_2O$  and  $H_2CO$ , respectively. Thus, selective epoxidation is limited to an upper temperature of approximately 50°C.

This results show that the use of  $H_2O_2$  as oxidant and TS-1 as catalyst is the best combination of oxidant and catalyst. The lower yield when  $H_2O_2$  is used with the Pt-Pd/TS-1 catalyst is due to the decomposition of some of the  $H_2O_2$  by the Pt-Pd part of the catalyst before it reacts with  $C_3H_6$ . The use of  $H_2 + O_2$  as the oxidant indicates that Pt-Pd is required for  $H_2O_2$  formation. The lower yield for propylene oxide using  $H_2 + O_2$  (5.3%) rather than  $H_2O_2$  (21.3%) suggests that formation of  $H_2O_2$  is rate limiting for propylene oxide formation.

In addition to the limitations of Pt-Pd/TS-1 to form  $H_2O_2$  at rates sufficient to have higher yields of propylene oxide, the simultaneous addition of  $H_2$  and  $C_3H_6$  and  $H_2$  and  $O_2$  in the presence of noble metal such as Pt and Pd leads to severe yield losses by formation of  $C_3H_8$  and  $H_2O$ , respectively. Holdreth has found that key to controlling reaction pathways to produce  $H_2O_2$  and, subsequently, propylene oxide is that the Pd crystallites must be highly dispersed and preferentially exist as small, needle-shaped aggregates, rather than the more typical large, spherical-shaped particles. Calcination and reduction procedures for the impregnated  $Pd(NH_3)(NO_3)_2$  and  $Pd(NH_3)_2(NO_3)_2$  salts were critical in determining the final shape (needle versus spherical), size, and surface oxidation state ( $Pd^0$  versus  $Pd^{2+}$ ) of the final Pd crystallites. Not unexpectedly, milder calcination (lower temperatures and lower  $O_2$  concentrations) and reduction (lower temperatures and lower  $H_2$  concentrations) conditions favored the formation of small, needle-shaped Pd aggregates that contained the largest fraction of surface  $Pd^{2+}$  sites. Because the concentration of surface sites correlated well with the formation rates of  $H_2O_2$ , the surface concentration of  $Pd^{2+}$  was viewed as critical in determining maximum activity for the formation of propylene oxide. The addition of minor amounts of Pt to Pt/TS-1 dramatically increased the concentration of  $Pd^{2+}$  relative to  $Pd^0$ . For 1 wt% Pt/TS-1 the addition of 0.01 and 0.02 wt% Pt increased the surface concentration of  $Pd^{2+}$  from 12% (no Pt) to 43 and 56%, respectively. Further increases in the amount of Pt up to 1.0% to give 1/1 weight ratios of Pt/Pd did not change the surface concentration of  $Pd^{2+}$ , but did change the shape of the Pd aggregates from primarily rod-shaped to a mixture of rod-shaped crystallites and the undesirable, spherical crystallites. Thus, the optimum level of Pt is a balance of increasing the

activate the  $H_2O_2$  for electrophilic addition to the C-C double bond of the substrate olefin. Holdreth and coworkers [20,21] have reported that propylene oxide can be produced using a bifunctional, heterogeneous catalyst composed of palladium supported on titanium silicate (TS-1), or more preferably, platinum-promoted, palladium supported on TS-1. The reaction, which is run as a liquid phase slurry reaction typically uses a mixture of methanol and water as the slurry liquid. This bifunctional composition uses Pd or Pt-promoted Pd to generate  $H_2O_2$  from the  $H_2$  and  $O_2$  which are present, along with propylene, in the feed. Once formed, the  $H_2O_2$  is activated by the appropriate  $Ti^{4+}$  sites on TS-1 support. Reaction of propylene with the activated hydroperoxide species then forms propylene oxide. The obvious benefits of this catalyst system and feed composition is that expensive  $H_2O_2$  is not required as the source of the hydroperoxide species, which is the oxidant for TS-1. Holdreth has examined the effects of different oxidants ( $H_2O_2$  versus  $H_2$  and  $O_2$ ) and catalyst compositions (TS-1 and Pt-Pd/TS-1) for the production of propylene oxide. Key results, taken from [21] are shown below in Table 2. The Pt-Pd/TS-1 catalyst was made using wet impregnation of an aqueous solution of  $Pd(NH_3)(NO_3)_2$  and  $Pt(NH_3)(NO_3)_2$  to give a composition of 0.1 wt% Pt-1.0 wt% Pd supported on TS-1. The catalyst precursor was then thermally reduced (by the  $NH_3$  ligands) by heating at 150°C for 1 h in flowing  $N_2$ . An autoclave charged with 0.2 bar and 1.5 g  $C_3H_6$  and 5 g  $H_2O$  was sealed and 10 g  $C_3H_6$  (0.24 mol) and 7 bar  $H_2$  (59 mmol), 10 bar  $O_2$  (92 mmol), and 15 bar  $N_2$  were used to pressure the reactor up to reaction conditions. When  $H_2O_2$  was used as the oxidant, 8 g of 30%  $H_2O_2$  were used in place of  $H_2$  and  $O_2$ .

Table 2  
Epoxidation of propylene

Oxidant	Catalyst	PO yield (%) based on $C_3H_6$ conversion and PO formed
$H_2O_2$	TS-1	38.3
$H_2 + O_2$	61 wt% Pt-1.0 wt% Pt/TS-1	21.3
$H_2 + O_2$	TS-1	0
$H_2 + O_2$	0.1 wt% Pt-1.0 wt% Pt/TS-1	5.3

Catalysts containing gold particles <2 nm diameter primarily formed  $C_3H_6$  from the selective hydrogenation of  $C_3H_4$ . Catalyst containing gold particles >4 nm in diameter were still selective for propylene oxide formation; however, the rate of formation, based on Au loading, decreased due to lower concentration of active Au sites as particle size increased. Formation of small, supported Au particles is accomplished by a deposition-precipitation technique, rather than the usual method of wet impregnation of a soluble gold salt, followed by calcination/reduction. Gold is deposited on the  $TiO_2$  surface by precipitation of  $Au(OAc)_3$  from a basic solution of chloroauric acid at pH = 7-10, onto the  $TiO_2$  support. After washing to remove the residual  $Cl^-$ , the catalyst was calcined at 400°C to form the gold particles. Only by using the deposition-precipitation technique could hemispherical Au particles with diameters between 2.0 and 4.0 nm be prepared.

Cheriet and Ingallina [22] has proposed the following mechanistic scheme in Fig. 1 to explain the features of these gold catalysts for the epoxidation of  $C_3H_4$ .

In this scheme,  $O_2$  is inserted into a bridged  $Ti^{IV}-Au^0$  site to form an activated molecular oxygen species. Reaction with  $H_2$  forms the hydroperoxy species, which after elimination of  $H_2O$ , gives the active oxygen species that reacts with  $C_3H_4$  to form propylene oxide, although the bridging hydroperoxy species could also selectively react with  $C_3H_4$  to form propylene oxide. The site for  $C_3H_4$  adsorption

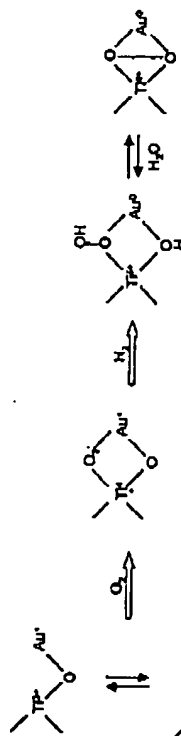


Fig. 1. Probable mechanism for the formation of the active oxygen species on  $Au/TiO_2$  catalyst.

observed in Cheriet and Ingallina's [22] work) is the strong adsorption of propylene oxide on the catalyst. The desorption of strongly-bound olefin epoxide products and the subsequent effects on catalyst design will be discussed in more detail when the epoxidation of higher olefins, such as 1,3-butadiene, over supported silver catalysts is discussed.

It is possible to calculate the upper limit of catalytically-active sites for supported  $Au/TiO_2$  catalysts. The 0.98 wt%  $Au/TiO_2$  catalyst evaluated and characterized by Cheriet and Ingallina [22] contained Au particles with a mean diameter (measured by transmission electron microscopy) of 2.4 nm. Using the solid state parameters from Anderson [35], we can calculate the dispersion of 2.4 nm Au particles to be 0.49. However, if only the interfacial Au sites are active (since the active site is postulated to be a bridged  $Ti^{IV}-Au^0$  species), then the effective dispersion of the Au particles decreases to 0.11. This gives an upper limit of the concentration of active sites, since not all the Au sites on the interfacial perimeter of Au and  $TiO_2$  will be coordinated to  $Ti^{IV}$  sites. The propylene oxide formation rate reported by Hanna was 0.20 mmol/(g Au), corresponding to  $3.34 \times 10^{16}$  PO molecules/(g Au). The above catalyst contained a maximum of  $3.2 \times 10^{18}$  Au sites/g Au, resulting in a turnover frequency for propylene oxide formation =  $0.01 s^{-1}$ . Turnover frequencies in this range are approximately 20-100 times lower than reported turnover frequencies reported for ethylene oxide and propylene formation and indicate one of the principal shortcomings of this catalyst system. Both  $C_3H_4$  conversion and space time yields of propylene oxide must be dramatically improved for this system to become commercially-viable. Other problems include catalyst deactivation, which may be partially due to yet another problem with supported Au catalysts, that of preventing particle sintering under reaction conditions.

Regardless, the potential of this route has reaction has attracted the attention of a number of chemical companies and patents have recently appeared claiming selective production of propylene oxide using gold supported on various  $Ti$ -containing supports [36-42]. Most of these patents are concerned with proprietary advances that claim higher space time yields of propylene oxide and longer catalyst lifetimes under reaction conditions. Although promoted silver catalysts normally used for ethylene epoxidation are virtually non-selective for propylene oxide formation due to the high reactivity of the allylic C-H bonds [43], a number of research efforts have shown that heavily-modified silver catalysts do show improved selectivity to propylene oxide. Compared to silver catalyst compositions used for ethylene oxide formation, these catalysts have much higher silver, alkali metal, alkaline earth, and chlorine loadings and, thus, are quite different in terms of

reaction conditions. For example, Bonneau and coworkers [40-42] have reported that supported  $Au/TiO_2$  catalyst systems can be used to epoxidize  $C_3H_4$  at 8% selectivity and 0.45% conversion of  $C_3H_4$  with a GHSV of  $1800 h^{-1}$ . The higher levels of  $C_3H_4$  conversion are attained by operation at 163°C. However, at these conditions, catalyst lifetime is limited, requiring frequent re-regeneration by calcination at high temperatures in air. Likewise, conversion of  $H_2$  is high, with excess generation of  $H_2O$ . For the above reaction conditions, the molar  $H_2O$ /propylene oxide ratio varied between 13 and 18, indicating that most of the  $H_2$  was oxidized to  $H_2O$  rather than  $H_2O_2$ .

### 3. Epoxidation using molecular oxygen

With few exceptions, all direct epoxidation reactions using  $O_2$  as the oxidant are heterogeneous, silver-based catalysts that are promoted to greater or lesser extent with alkali and/or alkaline earth promoter salts. Chlorine is also used as a reaction moderator, and the chlorine may be added either during preparation, or added during reaction conditions by decomposition of organic chlorides in the feedstream. Because of the importance and current volume of propylene oxide, almost all effort has focused on selective epoxidation of propylene. The recent demonstration that olefins larger than propylene, such as 1,3-butadiene, styrene, and norbornene, can also be epoxidized by silver, some attention toward these potentially-important reactions and chemical intermediates. The following discussion will first discuss the development and state of the art for propylene epoxidation, before the discussion of higher olefin epoxidation.

#### 3.1. Epoxidation of propylene

Although promoted silver catalysts normally used for ethylene epoxidation are virtually non-selective for propylene oxide formation due to the high reactivity of the allylic C-H bonds [43], a number of research efforts have shown that heavily-modified silver catalysts do show improved selectivity to propylene oxide. Compared to silver catalyst compositions used for ethylene oxide formation, these catalysts have much higher silver, alkali metal, alkaline earth, and chlorine loadings and, thus, are quite different in terms of



their physical and chemical properties. In some compositions, the modified silver composition is even unsupported. During preparation, the components of the catalyst are mixed into a liquid slurry, rather than being deposited using wet impregnation or incipient wetness methods onto a support, and then ball-milled to capture even mixing and distribution of components before drying and calcination. The catalyst work was reported by Kolombos and McChin [44] for a series of catalysts that were prepared by slurring silver powder with various group IIA metal halides, specifically  $MgCl_2$ ,  $CaCl_2$ , and  $BaCl_2$ , which after drying gave catalysts with the balance being a group IIA metal chloride. Evaluation of these catalysts at 240–280°C in a gas stream of 3%  $C_3H_6$ , 20–40%  $O_2$ , balance He gave selectivities to propylene oxide of 12–16%, at propylene conversions between 80 and 90%. While these results were clearly marginal, they were much better than propylene oxide selectivities for silver catalyst compositions used for ethylene oxide production.

Later work by Thorneisen [45] extended the study of heavily-modified, silver catalysts. A catalyst composed of 40 wt% Ag and 1.5 wt% K supported on or mixed with  $CaCO_3$  (which itself can be considered to be a promoter as well as a support) was exposed to a feedstream of 10%  $C_3H_6$ , 9%  $O_2$ , 200 ppm  $C_2H_5Cl$ , and balance  $N_2$  at 243°C. Propylene conversion was 34% at a selectivity to propylene oxide of 47%.

Llewellyn, Bowman [46] prepared and evaluated a series of catalysts characterized by having high weight loadings of Ag (approximately 60 wt% Ag) and promoted with high, but unspecified, loadings of group IIA salts and supported on sodium silicate. Among the different catalysts, performance of a Mg-promoted catalyst at 180°C in a flow stream of 68%  $C_3H_6$ , 29%  $O_2$ , and 3%  $H_2O$  vapor as a gas hourly space velocity (GHSV) = 2200  $h^{-1}$  gave a selectivity to propylene oxide = 47% at 3.7%  $C_3H_6$  conversion. However, the low GHSV needed to obtain 3.7% conversion underscores the low activity of this catalyst system.

The intrinsically low activity of these types of catalyst systems has been addressed by Lu and Zuo [47] for an unsupported Ag catalyst promoted with NaCl or  $BaCl_2$ . Reaction temperatures as high as 390°C at a GHSV of 24,000  $h^{-1}$  for a gas stream of 3%  $C_3H_6$ , balance air resulted in conversion of 54% of  $C_3H_6$  at 26% selectivity to propylene oxide. Even at these short

contact times, the selectivity is unusually high. The authors claim that NaCl and  $BaCl_2$  are better promoters than comparable loadings of  $NH_4Cl$  and LiCl, indicating that the catalyst performance is partially due to the  $Na^+$  and  $Ba^{2+}$  cations, not just the Cl<sup>-</sup> anion. Promoter loadings either lower or higher than 3.8–4.5%  $NaCl$  gave catalysts with lower activity and selectivity. Most of the reported work for oxidation of propylene by heavily-modified, high weight loading Ag catalysts have been carried out by Gaffney and coworkers [48–53]. Catalyst compositions investigated by Gaffney include the following components and ranges of composition: 30–60% Ag, 0.5–3% K, 0.5–1% Cl, 0.5–2.5% Mo, 0.5–1% Ba, 0.5–1% W, and balance  $CaCO_3$ . At these weight loadings of Ag and other moderators, it is not realistic to consider  $CaCO_3$  as a support, since in some cases it is a minority component. Shortages of the components with powdered  $CaCO_3$  are ball-milled, thoroughly mixing the  $CaCO_3$  with the other components. After drying and calcining, the powder is pressed and shaped into granules or other preferred shapes. Gas phase feed compositions were typically 10%  $C_3H_6$ , 5%  $O_2$ , optimally 5–25%  $CO_2$ , and balance  $N_2$  or other inert ballast gas, as well as 50–500 ppm organic halide, typically ethyl chloride, and 20–500 ppm NO. Most of the reactions were conducted at 250°C at 10 psig (3 bar) pressure at a total GHSV of 1200  $h^{-1}$ .

Gaffney showed that the complex recipe of catalyst components and gas phase promoters was required for both activity and selectivity to propylene oxide. Thus, a catalyst composed of 50 wt% Ag and 50 wt%  $CaCO_3$  gave only 3% selectivity to propylene oxide, while a catalyst with Ag, K, and  $CaCO_3$  without any organic chloride or NO feed promoter gave low conversion (<1%) and low selectivity (<3%). Co-feeding ethyl chloride and NO along with  $C_3H_6$  and  $O_2$  enhanced both conversion (up to 10%) and selectivity (up to 60%). The role of NO is poorly understood, although one hypothesis is that adding NO maintains a critical concentration of  $NO_2^-$  on the catalyst surface, although there is no explanation as to why  $NO_2^-$  is needed to enhance performance. The role of NO is further complicated by the observation that a catalyst containing Mo as a promoter has the same activity and selectivity with or without NO in the feed. The levels of ethyl chloride used with this process (typically about 200 ppm) are many times higher than the levels

currently used in either the epoxidation of ethylene or butadiene. In the latter case, typical levels of organic chloride in the feed vary between 1 and 3 ppm [54,55]; levels higher than 5–10 ppm would result in continuous loss of activity for ethylene oxide and epoxycyclohexanol.

Even though the performance of this catalyst system is better than for the other propylene epoxidation systems discussed above, the propylene oxide yield is still too low for commercial use. For a reported [49] activity of 2.2% conversion at 59% selectivity to propylene oxide using 2  $cm^3$  of catalyst at 30 psig and 245°C, the calculated space time yield is 0.7 kg propylene oxide/( $kg$  h), which is at least an order of magnitude lower than ethylene oxide and epoxycyclohexanol production rates.

It is very difficult to determine any kind of catalyst surface structure-catalyst performance correlation with these catalysts, since surface compositions of these complex catalysts are so poorly defined. Not only are the concentrations of Ag, K, Cl much higher than commonly used in propylene oxide catalysis, the catalyst components are not deposited onto the  $CaCO_3$  by wet impregnation or incipient wetness, but are actually thoroughly mixed with the  $CaCO_3$  during preparation. Thus, it is not possible to determine whether the  $CaCO_3$  functions primarily as a physical support, as a necessary component of the catalyst, or as a diluent for bulk silver.

If we consider these systems as a uniform mixture of silver and  $CaCO_3$ , the catalytic properties can be addressed in terms of the well-known ligand and ensemble effects of catalysts [56], whereby catalytic behavior is influenced by either the electronic properties of Ag sites interfused with  $CaCO_3$  (ligand effect), or by the sizes of contiguous arrays of Ag atoms that have different reactivity due to different size requirements (ensemble effect) for competing reactions. Ensemble effects are normally associated with metallic alloys, where the alloy surface can be theoretically diluted into ensembles of contiguous atoms of the catalytically-active component. It is not obvious that the type of atomic dilution inherent in ensemble theory is going to occur from physical mixing of a Ag salt and  $CaCO_3$ . Surface aggregates of Ag and  $CaCO_3$  resulting from mixing should be much larger than the 5–20 atom aggregates typically considered to be relevant in catalysis. In fact, a correlation of Ag ensemble size

for propylene oxidation over Ag-Au alloys has been carried out by Geniesse et al. [57], who found that for Ag-Au alloy surfaces that were rich in gold (>70% Au at surface),  $C_3H_6$  was selectively oxidized to acrolein (propenal); propylene oxide was produced only at trace amounts and did not change with the degree of gold alloying. The authors argued that while formation of propylene oxide did not exhibit an ensemble effect, the selective formation of acrolein indicated that small ensembles of Ag atoms were sufficiently large enough to effect the allylic oxidation of propylene to acrolein, but were too small to allow consecutive oxidation of acrolein to  $CO_2$  and  $H_2O$ . Concomitant required a larger number of Ag atoms to permit overlap of adsorbed acrolein with adjacent O-covered Ag atoms.

The more logical possibility for the selective activity of the catalysts prepared by Gaffney is the existence of selective sites at the interface of the Ag and  $CaCO_3$  portions of the catalyst. The need to further promote catalysts that are composed essentially of equal weights of Ag and  $CaCO_3$  with high levels of K and Cl to obtain selective behavior may be to effectively poison the conventional Ag sites existing on the surface of the exposed silver surface, leaving only the interfacial Ag- $CaCO_3$  sites. If this is the case, one major goal of catalyst development and potential area for future research should be directed to increasing the concentration of active and selective sites, since current catalysts have activities too low for commercial utility. Regardless, this family of catalysts should be considered as one of the more promising new systems for selective epoxidation of propylene to propylene oxide. Since almost all information regarding the structure and performance of this novel system exists in patents, this is one area that could greatly benefit from a detailed study of better characterized catalysts to help elucidate the nature of the active and selective sites for propylene oxide formation.

### 3.2. Epoxidation of 1,3-butadiene

Monoxide and co-oxides [3,35,58–64] have demonstrated that it is possible to selectively epoxidize higher alkenes to their corresponding epoxides using supported silver catalysts as long as the olefin does not contain reactive, allylic hydrogen atoms. Using an unpromoted Ag/ $\alpha-Al_2O_3$  catalyst, Mauer attempted

spectroscopy the thermal desorption products of butadiene adsorbed on an oxygen-saturated Ag(110) surface and concluded the desorption products were primarily 2,5-dihydrofuran and furan. In later thermal desorption studies of 1-butene from Ag(110) surfaces, Roberts et al. [32] concluded that 1-butene was oxidatively dehydrogenated to form 1,3-butadiene, which then underwent 1,4-addition to initially form 2,5-dihydrofuran. In agreement with the above results, Solent and Jorgensen [66] used extended Huckel calculations to determine the geometry of the interaction of butadiene on oxygen-covered Ag(110) planar surfaces and calculated that 1,4-addition of oxygen to form 2,5-dihydrofuran is thermodynamically favored over 1,2-addition to form epoxybutene. The mechanism of Madix and colleagues [67] for the formation of epoxybutene from butadiene on Ag(110) did not provide any reasonable pathway for the formation of epoxybutene. Previous results for oxidation of butadiene using supported silver catalysts corroborate the results of Madix and Jorgensen. Puthasanthi and Hest [67] and Rao [68] evaluated 10% Ag/BPO<sub>4</sub> and 70% Ag/MoO<sub>3</sub>, respectively, as catalysts for butadiene oxidation and found that, in both cases, the preferred oxidation product was furan which was formed by oxidation of 2,5-dihydrofuran as the primary product. Neither catalyst, however, was very active or selective for furan formation.

The difficulty with the above results is that the formation of epoxybutene is not satisfactorily explained. Thermodynamically, the isomerization of 2,5-dihydrofuran to form epoxybutene is unfavored by 19.5 kcal/mol. To determine which, if any, of the reaction pathways in Fig. 2 was dominant during butadiene epoxidation, realistic concentrations of each of

the reaction intermediates in Fig. 2 were sequentially added to the reactor feedstream during the epoxidation reaction. The results, which are shown in Table 4, indicate that (a) furan does not undergo further reaction, (b) 2,5-dihydrofuran is selectively oxidized to furan, (c) crotonaldehyde or 2-butenal, is only slightly oxidized to CO<sub>2</sub>/H<sub>2</sub>O, and (d) epoxybutene is not only converted to furan (via 2,5-dihydrofuran), nor butenol, crotonaldehyde, and CO<sub>2</sub>, only 55% of the epoxybutene which was added could be accounted for. Thus, epoxybutene was the only reaction intermediate that could account for all observed reaction products (and in the appropriate ratios) during butadiene epoxidation. Further, the net rate of epoxybutene formation was greatly suppressed during the period of time that epoxybutene was externally added to the reactor feedstream. This activity was slowly restored when epoxybutene was removed from the feed, indicating a strong kinetic inhibition by epoxybutene for the formation of epoxybutene. The strongly-bound epoxybutene was also the reason for poor accountability of epoxybutene when it was added to the feedstream.

The results from co-feeding of epoxybutene suggested that all reaction products could be satisfactorily explained by the direct 1,2-addition of oxygen to adsorbed butadiene to initially form epoxybutene. The strong adsorption of epoxybutene resulted in rearrangement to form 2,5-dihydrofuran and furan as well as the hydrolysis products, acrolein and formaldehyde; the strong adsorption also explained the kinetic inhibition effect of epoxybutene. Although the preference for 1,2-addition of oxygen to one of the localized C=C double bonds of butadiene is not predicted by the thermal desorption work of Madix,

cases of propylene and 1-butene, respectively), only CO<sub>2</sub> and H<sub>2</sub>O were formed. However, the results for butadiene indicated it was possible to epoxidize this non-allylic olefin to 3,4-epoxy-1-butene, the mono-epoxide of butadiene. However, after only 2-3h on line, catalytic activity declined from 2.8 to 0.6% conversion. Selectivity to epoxybutene also declined from 75 to 45% non-selective products (and selectivities to these products) changed from essentially CO<sub>2</sub> (25%) to a mixture of CO<sub>2</sub> (4%), furan (11%), acrolein (24%), 2-butenal (16%), and a trace of 2,5-dihydrofuran (<1%) with the added reaction time. The three-pronged mechanistic scheme summarized in Fig. 2 was formally used to explain the source of all reaction products. The formation of epoxybutene is shown as 1,2-electrophilic addition of oxygen across either of the C=C double bonds. Acid-catalyzed isomerization of epoxybutene forms 2-butenal [65], or crotonaldehyde, which is thermodynamically favored by 30.4 kcal/mol. Hydrogenolysis of the C<sub>3</sub>-C<sub>4</sub> bond of an unepoxidized C<sub>4</sub>-oxygenated intermediate provides a pathway for the formation of acrolein and formaldehyde, both of which were formed in approximately 1:1 molar ratios during the epoxidation reaction. Finally, the pathway for 1,4-addition of oxygen across the ends of butadiene initially forms 2,5-dihydrofuran, which undergoes facile allylic oxidation to give furan. The 1,4-addition route is the one favored by Roberts et al. [33] who analyzed by mass

Table 1  
Oxidation of olefins over unepoxidized 3% Ag/MoO<sub>3</sub><sup>a</sup>

Reaction	Selectivity (%)	Conversion (%)
CH <sub>3</sub> -CH=CH <sub>2</sub> + O <sub>2</sub>	41	12
CH <sub>2</sub> =CH-CH <sub>3</sub>	40	
CH <sub>3</sub> -CH=CH-CH <sub>3</sub> + O <sub>2</sub>		7
CH <sub>2</sub> =CH-CH=CH <sub>2</sub>	91	
CH <sub>3</sub> -CH=CH-CH <sub>3</sub>	8	
CH <sub>3</sub> -CH=CH-CH <sub>3</sub> + O <sub>2</sub>	91	8
CH <sub>3</sub> -CH=CH-CH <sub>3</sub>	9	
CH <sub>3</sub> -CH=CH-CH <sub>3</sub> + O <sub>2</sub>	98	1.2
CH <sub>3</sub> -CH=CH-CH <sub>3</sub> + O <sub>2</sub>	2	
Other	2	
CH <sub>3</sub> -CH=CH-CH <sub>3</sub> + O <sub>2</sub>	25	2.6
CH <sub>3</sub> -CH=CH-CH <sub>3</sub>	75	

<sup>a</sup> Reaction temperature = 250°C and butadiene = 1-butene  
olefin/O<sub>2</sub> = 2:1:1.

the epoxidation of a series of olefins. The results, summarized in Table 3, indicated that while the observed selectivity to ethylene oxide was expected for an unpoisoned catalyst, the selectivities to propylene oxide and butylene oxide were non-existent. In addition to small amounts of the selective allylic oxidation products (acrolein and butadiene in the

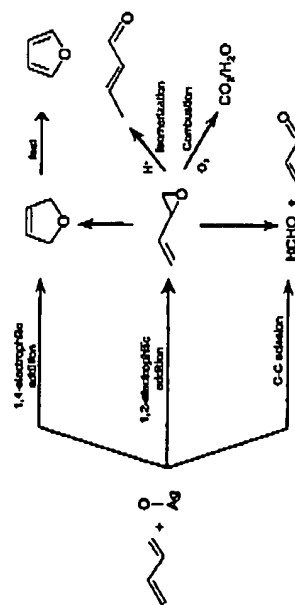


Fig. 2. Overall mechanistic scheme for C<sub>4</sub>H<sub>6</sub> epoxidation.

Table 4  
Addition of reaction products to feedstream during butadiene epoxidation

	Feed addition			
	Furan	Crotonaldehyde	2,5-DHF	Epoxybutene
Furan	N/A	0	75	4
Acrolein	0	0	0	0
2,5-DHF	0	0	N/A	0
Epoxybutene	0	0	0	N/A
Crotonaldehyde	0	N/A	6	25
CO <sub>2</sub>	0	4	16	14
Conversion of additive (%)	0	4	24	46
Accountability of additive (%)	100	100	97	55

one explanation for Madix' results is that the strong adsorption of epoxycyclohexane on the unpromoted (110) silver surface permitted rearrangement to the more thermodynamically stable 2,3-dihydronaphthalene, which resembles 1,4-addition. The actual geometry of the reaction intermediates during 1,2-addition is not known, although the intermediate is likely to be similar to that proposed during epoxidation of ethylene, which is considered to be concerted addition of an adsorbed oxygen atom across both carbon atoms of a C=C double bond. Alternatively, Burtens and coworkers [69,70] have used a combination of density functional theory (DFT) calculations and high resolution electron energy loss spectroscopy (HREELS) to conclude that all silver-catalyzed olefin epoxidation reactions proceed through unsaturated cyclic intermediates. For epoxycyclohexene formation, the terminal carbon atom of one of the C=C double bonds would be bonded to an oxygen atom which is adsorbed on a Ag site; the adjacent internal carbon would also be bonded, in this case to a Ag atom, giving a five-membered oxametallacycle. According to Madix and Burtens, ring closure and desorption of this intermediate forms epoxycyclohexene. This somewhat controversial intermediate and mechanism for olefin epoxide formation has re-initiated interest in the mechanism of olefin epoxidation.

Promotion of the unsupported catalyst by CuCl greatly improved activity, selectivity to epoxycyclohexene, and stability. Promotion by 100 ppm Cu (added as CuCl) increased conversion from 0.8 to 12.0% and selectivity from 45 to 92%. Catalyst lifetime increased from several hours to greater than the length of testing (24 h). Measurement of the apparent activation energy for epoxycyclohexene formation showed that  $E_{app}$  was lowered from 40.7 before promotion to 26.4 kcal/mol after promotion by CuCl. A different approach has been used by Boeck and coworkers [71,72] to maintain activity for silver catalysts used for butadiene epoxidation. The authors report that steam at concentrations between 6 and 80 mol% can be added to the reactor feed to lower the rate of fouling and, thus, increase lifetime. While lifetime is somewhat extended (catalyst must still be periodically regenerated by calcination), catalyst activity and selectivity remain unacceptably low, due to the inherent kinetic inhibition effect of epoxycyclohexene. The reported space time yield at 220°C and a GHSV of 250 h<sup>-1</sup> was 0.5 lbs epoxycyclohexene (ft<sup>3</sup>) catalyst at

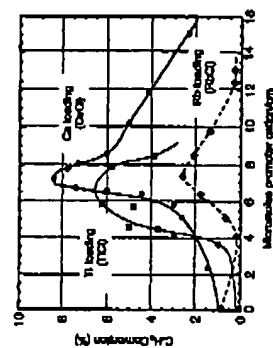


Fig. 1. Promoter loading vs. catalyst performance. Reaction temperature = 210°C, feed composition to  $\alpha$ -C<sub>6</sub>H<sub>10</sub>/C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> = 4:1:1 at GHSV = 5400 h<sup>-1</sup>. Selectivity to epoxycyclohexene in optimum loading: CuCl = 94.3%, RbCl = 91.5%, TICl = 90.0%.

a selectivity of 82-84%, which is much lower than the results reported by Moenier et al. The long-term effects of water in the presence of epoxycyclohexene at reaction temperatures are also questionable since it is known that epoxycyclohexene is hydrolyzed by water to form 3-hydroxy-1,2-diol [73], which has physical and chemical properties that might lead to even more deactivation than epoxycyclohexene alone.

The curves in Fig. 3 show that promotion by CuCl gives a maximum activity at approximately 950 ppm Cu, or 2.0  $\mu$ mol Cu/l, for this family of supported silver catalysts. Likewise, promotion by RbCl and TICl also indicate that loadings of approximately 7-8  $\mu$ mol Rb and Tl/g<sub>Ag</sub> result in maximum activity for epoxycyclohexene formation. Catalysts promoted by CuCl over the same concentration range did not exhibit similar enhancements in either activity or selectivity; performance was essentially the same as for unpromoted catalysts. Reaction conditions for the promoted 12 wt.% Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst in all cases were 1 bar pressure and 210°C using a feed composition of  $\alpha$ -C<sub>6</sub>H<sub>10</sub>/C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> = 4:1:1 at a GHSV of 5400 h<sup>-1</sup>. It is interesting to note that optimum promoter loadings of Rb, Cu, and Tl all occur at similar molar loading levels, suggesting a specific and common type of interaction (rather than random deposition of promoter) of the promoter with the silver surface. That the interaction

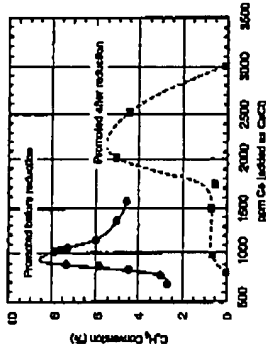


Fig. 4. Effect of Ag salt reduction on promoter efficiency. Reaction temperature = 210°C, feed composition to  $\alpha$ -C<sub>6</sub>H<sub>10</sub>/C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> = 4:1:1 at GHSV = 5400 h<sup>-1</sup>.

of the promoter salts occurs with the silver surface, and not the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support, can be inferred from the curves in Fig. 4 for two series of catalysts which have been promoted at different stages of preparation. The sample promoted before reduction of the Ag salt precursor shows a sharp maximum at approximately 950 ppm Cu, while the sample promoted by Cu after reduction of the silver salt to Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> yields a broad maximum between 2000 and 2500 ppm Cu. The location of the optimum promoter loading at higher Cu loadings suggests that the Cu is deposited on both the Ag and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surfaces of the catalyst, while in the case of co-deposition of the Ag and Cu salt, the Cu is targeted much more effectively onto the Ag surface. Likewise, the interaction of the Cu promoter appears to be more effective when deposited before reduction of the Ag salt, since butadiene conversions are substantially higher (8% conversion versus 3.5% conversion, respectively), when the promoter is added before reduction.

Selected physical and electronic properties of different promoter cations are summarized in Table 5. The Cu<sup>+</sup>, Rb<sup>+</sup>, and Tl<sup>+</sup> salts that have shown positive promoter effects for epoxycyclohexene formation have cations that are large and highly polarizable [74]. In fact, the ionic radii and the values of the Pauling electronegativity of Cu<sup>+</sup>, Rb<sup>+</sup>, and Tl<sup>+</sup> are the largest of any of the naturally-occurring elements. Thus, the suc-

Table 5  
Properties of promoter cations for heterogeneous epoxidations

Cation (+)	Ionic radius (Å)	Charge/valence	Polarizability (Å <sup>3</sup> )
Lithium	0.78	0.130	0.03
Sodium	0.98	0.081	0.03
Potassium	1.33	0.045	1.18
Rubidium	1.49	0.035	1.98
Cesium	1.65	0.030	2.98
Thallium	1.40	0.040	4.18
Silver	1.36	-	-

cessful promoters are large and highly polarizable ions under reaction conditions. As stated above, catalysts promoted by K<sup>+</sup> salts are not active for epoxycyclohexene formation, suggesting that ionic size is not the critical factor in determining promoter efficiency. If promoter function merely by blocking, or neutralizing, non-selective sites, then K should show some promoter effect for epoxycyclohexene formation, based on size and reactivity of alkali metals. Polarizability, or the measure of an ion's ability to deform its electronic core to external electric fields, may be a more important factor in determining promoter efficiency than ionic size alone.

For catalysts optimized for epoxycyclohexene production, the 900-1000 ppm level of Cu loading is substantially higher than the 200-300 ppm Cu loadings typically used for ethylene oxide formation [75]. In fact, a catalyst optimized for epoxycyclohexene formation is essentially inactive for ethylene oxide, while a catalyst optimized for ethylene oxide formation is inactive for epoxycyclohexene [3]. These results clearly indicate the impact of differences in kinetics on promoter requirements for otherwise similar reactions. For epoxycyclohexene formation, the rate limiting step involves desorption of epoxycyclohexene [3], while for ethylene oxide formation, the rate determining step is considered to be the surface reaction between adsorbed ethylene and adsorbed oxygen [54]. However, for both reactions, the active oxygen used to form the epoxide is atomic oxygen [76,77], and not molecular oxygen [54]. Application of the 4/7 rule that has been used to rationalize the role of molecular oxygen in ethylene epoxidation would limit the selectivity of epoxycyclohexene to 11/12, or <91.7%. Selectivity values >91.7%, and as high as 94-96%, have been reported in Moenier and coworkers [58-64] with

### 3.3. Epoxidation of higher olefins

In addition to butadiene, Monnier has reported the selective epoxidation of higher non-allylic olefins such as styrene [78] and 3,3-dimethyl-1-butene [83] and hindered allylic olefins, such as norbornene [79], using Cu- and Ru-promoted, silver catalysts; results are summarized in Table 6. The data for the epoxidation of styrene and 4-vinylpyridine show that these catalysts are both active and selective for the formation of their respective epoxides and carbonyl species work by Blum [80] for supported silver catalysts and by Huetz et al. [76] for temperature-programmed reaction spectroscopy of styrene adsorbed on oxygen-covered Ag(111) single crystal surfaces. However, in the examples of Blum,

weight loadings of Na, K, Li, and Cs between 7000 and 60,000 ppm/area were used to promote the supported silver catalysts for the epoxidation of styrene. Thus, a catalyst having a composition of 39,800 ppm K (3.98%) and 16.8% Ag supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> exposed to a stream of 70% O<sub>2</sub>, 7% styrene, and 23% N<sub>2</sub> at 284 °C gave 13% conversion of styrene and a selectivity to styrene oxide of 83% at a GHSV of 1200 h<sup>-1</sup>. Conversely, the promoter loadings reported by Monnier ranged from 435 to 2620 ppm for Ru promoted compositions and 345-1330 ppm for Cu-promoted, silver catalysts. For both families of promoted catalysts, catalytic activities passed through a maximum at the intermediate promoter loadings of Ru and Cu. A catalyst with a composition of 1000 ppm CuNO<sub>3</sub> (680 ppm Cu) and 15% Ag sup-

Table 6  
Epoxidation of other olefins using CuCl-promoted, Ag/Al<sub>2</sub>O<sub>3</sub> catalysts

Reaction	Molar selectivity (%)	Conversion (%)
	95	19
	93	21
	0	100
	95	6.5
	92	43
	36	4

ported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> that was exposed to a stream of 10% O<sub>2</sub>, 3% styrene, and 88% He at 3600 h<sup>-1</sup> gave velocity and 230 °C gave 65% conversion of styrene at a selectivity to styrene oxide of 93%. It is not obvious why the catalysts evaluated by Blum contained much higher levels of promoter salts; no data were included for catalysts with lower promoter loadings. The results in Table 6 indicate that the presence of the *para*-CH<sub>3</sub> group in 4-vinylpyridine results in combustion of this olefin to CO<sub>2</sub>/H<sub>2</sub>O. While the -CH<sub>3</sub> group is not allylic in the vinyl group, it is both allylic and benzylic to the aromatic ring and is very reactive towards C-H bond breaking during oxidation. This reactivity and subsequent combustion of 4-vinylpyridine prevents formation of the epoxide. *Tert*-butyl ethylene, another non-allylic olefin in Table 6, is also very selectively epoxidized; however, the bulky *tert*-butyl group lowers reactivity of this olefin.

The results for epoxidation of norbornene in Table 6 indicate that Cu-promoted, silver catalysts also selectively epoxidize allylic olefins to their corresponding epoxides, as long as the allylic C-H groups are kinetically non-reactive. The results for norbornene agree well with the temperature-programmed reaction spectroscopy results of Roberts and Madix [77], who observed that norbornene epoxide desorbed at approximately 310 °K from a Ag(110) surface which had been pre-adsorbed with norbornene and atomic oxygen. In a related study, Cant et al. [81] reported that during continuous oxidation of norbornene by molecular oxygen over an unpromoted silver sponge catalyst only benzene was formed as the oxidation product. The authors concluded that norbornene oxide was not an intermediate during formation of benzene. Data from Monnier and Muehlbauer [79] for unpromoted silver catalysts confirm that only trace amounts of norbornene oxide are produced by unpromoted catalysts, but that Cu-promoted, silver catalysts are very active and selective for epoxide formation. The results of Cant are consistent with norbornene epoxide being the primary product, but that the strongly-bound norbornene epoxide undergoes hydrolysis and oxidative dehydrogenation to form benzene, in a manner analogous to acrolein and furan formation during oxidation of butadiene over unpromoted silver catalysts.

The importance of ensuring that olefins contain no reactive, allylic C-H bonds is seen by comparing the

selectivity differences between epoxidation of norbornene and bicyclo[2.2.2]oct-2-ene. Epoxidation of bicyclo[2.2.2]oct-2-ene is only 36% selective to the desired epoxide. The addition of the additional -CH<sub>2</sub> group in the bridging position results in a dramatic decrease in selectivity, presumably because the less puckered geometry of bicyclo[2.2.2]oct-2-ene makes the allylic hydrogen more accessible and reactive with the Ag-O surface. It is not possible to state whether the more favorable C-H bond angle of the allylic C-H bond, or the lower strain energy of the allylic structure (after C-H bond rupture), are responsible for the lower observed selectivity to the olefin epoxide. However, comparison of these two bicyclic olefins toward olefin epoxidation does underscore the importance of having no reactive, allylic C-H bonds for selective epoxidation to occur using supported silver catalysts.

### 4. Conclusions

Recent developments in olefin epoxidation have indicated it is possible to epoxidize higher olefins directly by using molecular oxygen, or indirectly, by using molecular oxygen to generate an active and selective oxidant *in situ* during reaction. The commonly-practiced methodology of syntomatic and minor modifications of pre-existing catalysts and technology in this case, the epoxidation of ethylene, have not been successful in advancing olefin epoxidation. In each instance of successful epoxidation of higher olefins, discontinuous changes from traditional approaches have been required. One novel approach has recognized that while it is known that H<sub>2</sub>O<sub>2</sub> is active and selective for epoxidation, the high cost of H<sub>2</sub>O<sub>2</sub> has prevented its use as a practical oxidant. However, the *in situ* generation of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> under olefin epoxidation reaction conditions is a potentially inexpensive way to combine H<sub>2</sub>O<sub>2</sub> with conventional olefin epoxidation catalysts, with as TS-1 and TiO<sub>2</sub>. These bifunctional catalysts have combined new catalyst components that generate H<sub>2</sub>O<sub>2</sub> *in situ* with the functional component that activates H<sub>2</sub>O<sub>2</sub> for olefin epoxidation. Generation of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> is a difficult research problem, especially in the presence of an olefin. Not only one must be concerned with selective use of H<sub>2</sub> and O<sub>2</sub> to generate H<sub>2</sub>O<sub>2</sub>, and not H<sub>2</sub>O, the competing hydrogenation reaction of the

olefin to form the corresponding paraffin is another facile reaction that must be suppressed. Current bifunctional catalysts use either a combination of noble metal components, such as Pt-Pd, to generate  $H_2O_2$ , or the unique properties of small supported gold particles to generate  $H_2O_2$ . In both cases, the primary limitations of these bifunctional catalysts are the low rates of  $H_2O_2$  formation (and subsequent low rates of olefin epoxide formation) and the non-selective consumption of  $H_2$  (which generates  $H_2O$ ) and olefins (which generate paraffins). Other problems include stability of these bifunctional compositions under reaction conditions and the potential flammability hazards associated with handling gas mixtures containing both  $H_2$  and  $O_2$ .

Another novel approach employs silver-based methodology, but in much different combinations of weight loadings of silver, promoters, and support than typically used for ethylene oxide catalysts. These catalysts, which have been used for propylene epoxidation, have much higher silver, alkali metal, alkaline earth, and chlorine loadings than the analogs used for ethylene oxide formation, and are quite different in terms of their physical and chemical properties. The silver and promoters are not supported to these compositions, but are actually uniformly mixed with the carrier, typically alkaline earth carbonates, such as  $CaCO_3$ . In some compositions, the modified silver composition is even unsupported. While the selectivities to propylene oxide are considerably higher than with conventional silver catalysts, selectivities and rates of olefin epoxide are still too low for commercial application. However, the improved performance of these catalysts is noteworthy. Since almost all information regarding the structure and performance of this novel system exists in patents, this is an area that could greatly benefit from a detailed study of better characterized catalysts to help elucidate the nature of the active and selective sites for propylene oxide formation.

Yet another approach has been to use silver-based catalysts for the selective epoxidation of non-allylic olefins, recognizing that the reactivity of allylic hydrogens makes the use of conventional silver-based catalysts unrealistic. Although the kinetic slow step for epoxidation of higher, non-allylic olefins is different from that for ethylene epoxidation, changes in the promoter loading levels have permitted the selective

epoxidation of olefins such as 1,3-butadiene, styrene, and kinetically hindered olefins, such as norbornene. This has led to the commercialization of butadiene epoxidation to form epoxybutene, the first olefin epoxide to be commercially produced since ethylene oxide was commercialized.

In summary, direct olefin epoxidation by molecular oxygen is an extremely important class of catalytic reaction. The recent examples of progress discussed in this article indicate that there is much left to exploit in direct epoxidation of higher olefins. Many of the compositional and structural features of these novel catalysts are poorly understood. Likewise, many of the kinetic features and reaction intermediates of higher olefin epoxidation remain to be elucidated. There are areas of catalytic research that, if successful, would have tremendous implications on growth of the chemical process industry as a whole when many believe that the chemical industry is mature. Olefin epoxides as a class of chemical compound are arguably one of the most versatile families of chemicals produced today.

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#### References

- [1] Chemical and Engineering News, 28 June 1999, p. 32.
- [2] Chemical and Engineering News, 21 August 1995, p. 7.
- [3] J.R. Monnier, *Synth. Ind. Catal.* 110 (1997) 133.
- [4] J. A. Dean, *Lange's Handbook of Chemistry*, McGraw-Hill, New York, 1973, p. 423.
- [5] C.T. Kinsley, M.J. Litt, A.C. Hegginson, D.R. Shime, *Can. J. Chem.* 36 (1978) 131.
- [6] S.-H. Woo, *Angew. Chem.* 106, 1994, p. 24.
- [7] M. Thomas, O. Kuch, R. Nuss, *US Patent* 4,416,501 (1983) to Shell.
- [8] B. Nuss, *Synth. Ind. Catal.* 110 (1997) 243.
- [9] M.G. Christ, G. Rothau, U. Reussner, *J. Catal.* 129 (1991) 139.
- [10] R.A. Buehler, J.K. Kochi, *J. Org. Chem.* 41 (1976) 1364.
- [11] L. Rosenthal, M. De Paure, *J. Catal.* 14 (1969) 114.

- [12] H.J. Clark, J.L. Miel, R.D. Bowman, S.R. Ben, O.E. Hermsrud, *WO Appl.* 94/00415 (1998) to Dow Chemical Company.
- [13] M.A. Bianchi, R.J. Mader, J. Am. Chem. Soc. 103 (1981) 344.
- [14] A.J. Kolambas, C.C. McCullo, *British Patent* 1,371,497 (1973) to British Petroleum Chemicals Limited.
- [15] B.M. Thompson, *Canadian Patent* 1,245,772 (1991) to Union Carbide Corporation.
- [16] R.D. Bowman, *US Patent* 4,841,551 (1989) to Dow Chemical Company.
- [17] Q. Lu, X. Zuo, *Chem. Lett.* 38 (1999) 67.
- [18] R. Prider, A.P. Kahn, A.M. Duffing, *US Patent* 5,621,084 (1997) to ARCO Chemical Technology LP.
- [19] R. Prider, A.P. Kahn, A.M. Duffing, *US Patent* 5,616,100 (1997) to ARCO Chemical Technology LP.
- [20] A.M. Duffing, G.A. Jones, R. Prider, A.P. Kahn, *US Patent* 5,699,214 (1997) to ARCO Chemical Technology LP.
- [21] A.M. Duffing, R. Prider, *US Patent* 5,702,834 (1997) to ARCO Chemical Technology LP.
- [22] B. Chabot, A.M. Duffing, J.D. Jones, R. Kahn, R. Prider, *US Patent* 5,770,244 (1998) to ARCO Chemical Technology LP.
- [23] B. Chabot, A.M. Duffing, J.D. Jones, A.P. Kahn, W.H. Olinick, *US Patent* 5,780,657 (1998) to ARCO Chemical Technology LP.
- [24] W.M.H. Sachter, C. Bruck, R.A. Van Santen, *Chem. Rev.* 351 (1981) 127.
- [25] J.R. Monnier, P.J. Mankabauer, *US Patent* 4,950,773 (1990) to Eastman Chemical Company.
- [26] W.M.H. Sachter, R.A. Van Santen, *J. Catal.* 26 (1977) 69.
- [27] P.V. Gnanou, H.J. Shaw, O.T. Fox, *J. Catal.* 17 (1983) 469.
- [28] J.R. Monnier, P.J. Mankabauer, *US Patent* 4,871,608 (1990) to Eastman Chemical Company.
- [29] J.R. Monnier, P.J. Mankabauer, *US Patent* 5,146,077 (1992) to Eastman Chemical Company.
- [30] J.R. Monnier, P.J. Mankabauer, *US Patent* 5,081,096 (1992) to Eastman Chemical Company.
- [31] C. Serres, H. Kretsch, O.M. Krich, H. Krich, O.L. Olinick, *US Patent* 5,162,801 (1994) to Eastman Chemical Company.
- [32] Q.L. Olson, J.R. Monnier, *US Patent* 5,503,043 (1999) to Eastman Chemical Company.
- [33] S.D. Boudreau, J.R. Monnier, K.J. Peters, *US Patent* 5,941,550 (1999) to Eastman Chemical Company.
- [34] S.D. Boudreau, J.R. Monnier, *US Patent* 6,001,161 (2000) to Eastman Chemical Company.
- [35] R.J. Crawford, S.B. Lerner, R.D. Cockland, *Can. J. Chem.* 34 (1976) 2164.
- [36] B. Schlatter, R.A. Ingrasano, *J. Phys. Chem.* 99 (1995) 10724.
- [37] R. Pordacchini, E.V. Kori, *US Patent* 4,291,444 (1981) to OAP Corporation.
- [38] V.N.M. Rao, *US Patent* 4,194,997 (1984) to E. I. DuPont de Nemours and Company.
- [39] J.W. Medlin, M.A. Bensen, *Oxometallics: Intermetallics in catalytic chemistry: a combined theoretical/experimental approach*, in: *Proceedings of the Annual Meeting of the American Institute of Chemical Engineers*, Houston 1999, Precedence no. 25.
- [12] H.J. Clark, J.L. Miel, R.D. Bowman, S.R. Ben, O.E. Hermsrud, *WO Appl.* 94/00415 (1998) to Dow Chemical Company.
- [13] M.A. Bianchi, R.J. Mader, J. Am. Chem. Soc. 103 (1981) 344.
- [14] A.J. Kolambas, C.C. McCullo, *British Patent* 1,371,497 (1973) to British Petroleum Chemicals Limited.
- [15] B.M. Thompson, *Canadian Patent* 1,245,772 (1991) to Union Carbide Corporation.
- [16] R.D. Bowman, *US Patent* 4,841,551 (1989) to Dow Chemical Company.
- [17] Q. Lu, X. Zuo, *Chem. Lett.* 38 (1999) 67.
- [18] R. Prider, A.P. Kahn, A.M. Duffing, *US Patent* 5,621,084 (1997) to ARCO Chemical Technology LP.
- [19] R. Prider, A.P. Kahn, A.M. Duffing, *US Patent* 5,616,100 (1997) to ARCO Chemical Technology LP.
- [20] A.M. Duffing, G.A. Jones, R. Prider, A.P. Kahn, *US Patent* 5,699,214 (1997) to ARCO Chemical Technology LP.
- [21] A.M. Duffing, R. Prider, *US Patent* 5,702,834 (1997) to ARCO Chemical Technology LP.
- [22] B. Chabot, A.M. Duffing, J.D. Jones, R. Kahn, R. Prider, *US Patent* 5,770,244 (1998) to ARCO Chemical Technology LP.
- [23] B. Chabot, A.M. Duffing, J.D. Jones, A.P. Kahn, W.H. Olinick, *US Patent* 5,780,657 (1998) to ARCO Chemical Technology LP.
- [24] W.M.H. Sachter, C. Bruck, R.A. Van Santen, *Chem. Rev.* 351 (1981) 127.
- [25] J.R. Monnier, P.J. Mankabauer, *US Patent* 4,950,773 (1990) to Eastman Chemical Company.
- [26] W.M.H. Sachter, R.A. Van Santen, *J. Catal.* 26 (1977) 69.
- [27] P.V. Gnanou, H.J. Shaw, O.T. Fox, *J. Catal.* 17 (1983) 469.
- [28] J.R. Monnier, P.J. Mankabauer, *US Patent* 4,871,608 (1990) to Eastman Chemical Company.
- [29] J.R. Monnier, P.J. Mankabauer, *US Patent* 5,146,077 (1992) to Eastman Chemical Company.
- [30] J.R. Monnier, P.J. Mankabauer, *US Patent* 5,081,096 (1992) to Eastman Chemical Company.
- [31] C. Serres, H. Kretsch, O.M. Krich, H. Krich, O.L. Olinick, *US Patent* 5,162,801 (1994) to Eastman Chemical Company.
- [32] Q.L. Olson, J.R. Monnier, *US Patent* 5,503,043 (1999) to Eastman Chemical Company.
- [33] S.D. Boudreau, J.R. Monnier, K.J. Peters, *US Patent* 5,941,550 (1999) to Eastman Chemical Company.
- [34] S.D. Boudreau, J.R. Monnier, *US Patent* 6,001,161 (2000) to Eastman Chemical Company.
- [35] R.J. Crawford, S.B. Lerner, R.D. Cockland, *Can. J. Chem.* 34 (1976) 2164.
- [36] B. Schlatter, R.A. Ingrasano, *J. Phys. Chem.* 99 (1995) 10724.
- [37] R. Pordacchini, E.V. Kori, *US Patent* 4,291,444 (1981) to OAP Corporation.
- [38] V.N.M. Rao, *US Patent* 4,194,997 (1984) to E. I. DuPont de Nemours and Company.
- [39] J.W. Medlin, M.A. Bensen, *Oxometallics: Intermetallics in catalytic chemistry: a combined theoretical/experimental approach*, in: *Proceedings of the Annual Meeting of the American Institute of Chemical Engineers*, Houston 1999, Precedence no. 25.

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- 91
- [70] J.W. Medlin, M. Marmakos, M.A. Barrow, *J. Polym. Chem.* **33** (1995) 111-119.
- [71] S. Bock, K. Kuroda, H. Fischer, H. Vogel, Martin Fischer, US Patent 5,618,914 (1997) to BASF Aktiengesellschaft.
- [72] S. Bock, K. Kuroda, H. Fischer, H. Vogel, Martin Fischer, US Patent 5,693,161 (1999) to BASF Aktiengesellschaft.
- [73] P.B. Mackenzie, J.A. Kari, S.M. Eiling, US Patent 5,236,391 (1999) to Chemical Company.
- [74] B.E. Douglas, D.H. McDermid, *Osorego and Models of Isoprene Chemistry*, Butterfield, Woburn, MA, 1985, pp. 102-113, 145-148.
- [75] A.M. Lauritzen, US Patent 4,761,294 (1989) to Shell Oil Company.
- [76] S. Koster, C. Malmik, J.S. Budge, R.M. Lambert, *Surf. Sci.* **115** (1982) 149-151.
- [77] J.R. Munnier, R.L. Munnier, *J. Am. Chem. Soc.* **110** (1988) 5440.
- [78] J.R. Munnier, P.J. Muehleberg, US Patent 5,145,566 (1992) to Eastman Chemical Company.
- [79] J.R. Munnier, P.J. Muehleberg, *WTU Appl.* 5041279 (1999) to Eastman Chemical Company.
- [80] P.R. Blum, US Patent 4,894,467 (1990) to The Standard Oil Company.
- [81] M.W. Cox, B.M. Kennedy, M.J. O'Leary, *Can. Lett.* **9** (1991) 113.